

Influence of Soil pH and Contents of Organic Carbon and Clay on the Volatilization of [^{14}C]Fenpropimorph after Application to Bare Soil

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Abstract: The behaviour of the morpholine fungicide fenpropimorph applied to soil was investigated in a laboratory chamber. The volatility and metabolism of a ^{14}C -labelled fenpropimorph formulation (Corbel®) was studied after application to three soils (sandy loam, loamy clay and loamy sand), simulating a four-day weather scenario in the volatilization chamber. Additional experiments were conducted under standard climatic conditions over a period of 24 h using sandy soils with different pH values. The results of the first experiments showed that most of the radioactivity applied remained in the soils as unchanged fenpropimorph four days after application. In the experiments with the sandy loam and loamy clay, less than 5% of the applied radioactivity was removed by volatilization whereas 11.4% volatilized from the surface of the loamy sand. The comparatively higher volatilization of the fungicide from the loamy sand was confirmed by the later experiments indicating that higher soil pH favoured volatilization of [^{14}C]fenpropimorph from sandy soils. Thus 5.6% (pH 5.0), 18.9% (pH 5.8) and 28.3% (pH 6.6) of the radioactivity applied volatilized within one day after application. The overall recoveries were between 93.8% and 111.3% in these experiments. © 1998 SCI

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Key words: volatilization; laboratory studies; simulated outdoor conditions; tracer technique; fenpropimorph

1 INTRODUCTION

The systemic morpholine fungicide fenpropimorph ('Corbel®') has been widely used for the control of *Erysiphe graminis* DC, *Rhynchosporium secalis* (Oudem) Davis and *Puccinia* spp. in crops since its introduction in 1979. Fenpropimorph is rapidly metabolized in cereals,¹ but can also reach the soil during spray application and as a result of wash-off after rainfall or formation of dew. Laboratory experiments in a closed volatilization chamber as previously described² can therefore provide information on the volatilization and degradation behaviour of [^{14}C]fenpropimorph applied to bare soils. In this chamber, experiments under standard climatic conditions can be carried out in addition

to experiments under simulated outdoor conditions.³ Using the radiotracers, mass balances are possible and the results obtained are reproducible.⁴ Established analytical methods such as HPLC in combination with the ^{14}C -tracer technique also result in low detection limits for the pesticide residues in soil and air.

Since it is well known that the degradation and volatilization rates of pesticides from soil surfaces depend on the soil properties such as pH, soil moisture, clay and organic carbon content,^{5,6} the fungicide was applied to different topsoils. To assess the influence of climate, field-like weather conditions were simulated in the volatilization chamber in terms of wind speed, air humidity, air temperature and solar irradiation measured during outdoor experiments with fenpropimorph reflecting a

typical climate of the main application time of the fungicide. In a second set of experiments, the volatilization of [^{14}C]fenpropimorph was measured under standard climatic conditions from loamy sand with different pH values.

2 MATERIAL AND METHODS

Physicochemical data for fenpropimorph [(\pm)-*cis*-4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine] are given in Table 1. The labelling position was at the phenyl ring. The radiochemical purity was between 92% and 97% and the specific activity was 3400 kBq mg $^{-1}$.

In the laboratory volatilization experiments, to allow for application losses, 1.1 times the recommended application rate was applied with a specific radioactivity of 76 kBq mg $^{-1}$ (experiments with different soils) and 30 kBq mg $^{-1}$ (experiments with the same soil but different pH values). The application losses consisted of side-wall contamination in the application chamber and contamination of the spraying system. The losses were determined after extraction with methanol of the paper covering the side walls and of the spraying system. The total amount applied to the bare soils was calculated by subtracting the losses from the total radioactivity used for application. The soils were filled into experimental platforms (0.5 m 2 surface area, 5 cm deep) and sprayed (nozzle type: Tee-Jet E 8001, spray pressure: 2.0 bar) with dilutions of fenpropimorph 750 g litre $^{-1}$ EC ('Corbel') to which the appropriate amount of [^{14}C]-labelled AI had previously been added. The designed amount of AI was 750 g ha $^{-1}$ and the amount of water was 400 litre ha $^{-1}$.

In the volatilization chamber (Fig. 1), the climatic conditions measured directly over plants in outdoor experiments were exactly simulated using an air-conditioning system (GEA Happel Klimatechnik GmbH) in the first experiments (Fig. 2). In this context, a computer-controlled lighting system (K. H. Steuernagel plc) was constructed above the volatilization chamber.⁸ The light intensities were reduced during the four-day studies with different soils in accordance with comparative measurements of solar irradiation in and over the plants. Since the pH-dependent volatilization of fenpropimorph from sandy soils was the focus of attention in the second set of experiments, the less costly and time-consuming one-day experiments with standard climatic conditions were carried out (20°C air temperature, 50% relative air humidity, 1.0 m s $^{-1}$ wind speed above the soil, no lighting). During the experiments, the air temperature, using a jacketed thermocouple (type 65250, Phillips plc), the relative air humidity, using a sensor (type 0555 6020 109, Testo plc), and the wind speed, using a thermal anemometer (type 8450, TSI Inc.), were recorded.

Furthermore, in all experiments an irrigation system was integrated into the topsoils to adjust the soil moisture to 50% of the maximum water-holding capacity (WHC $_{\text{max}}$) in order to obtain comparable results.

Shortly after application, the experimental platform was transferred to the volatilization chamber where the conditioned air streamed over the soil surface. At the end of the measuring system the air was passed through a filter which absorbed the radioactive compounds and a blower for discharging the air. A part of the total air stream (> 5%) was taken for further analysis: the air was separated into volatilized active ingredient and apolar metabolites adsorbed on polyurethane foams (PU-foams type T30150, Recticel Germany plc), polar

TABLE 1
Physicochemical Data of [^{14}C]Fenpropimorph^a and Soil Details

Mol. weight	303.5
Vap. pressure	3.5 mPa at 20°C
Water solubility	4.3 mg litre $^{-1}$ (pH 7, 22°C)
Henry's Law const.	1.0 $\times 10^{-7}$
pK $_{\text{a}}$	6.98
Soil types	<i>Experiments with different soils:</i>
	Sandy loam (pH 6.7, C $_{\text{org}}$ 1.5%, clay 13%, K $_{\text{OC}}$ 2875, WHC $_{\text{max}}$ ^b = 43 g/100 g)
	Loamy sand (pH 6.1, C $_{\text{org}}$ 0.8%, clay 7%, K $_{\text{OC}}$ 2125, WHC $_{\text{max}}$ = 36 g/100 g)
	Loamy clay (pH 6.8, C $_{\text{org}}$ 1.1%, clay 29%, K $_{\text{OC}}$ 2345, WHC $_{\text{max}}$ = 39 g/100 g)
	<i>Experiments with the same soil but different pH:</i>
	Loamy sand (pH 5.0, C $_{\text{org}}$ 0.9%, clay 3%, K $_{\text{OC}}$ 2125, WHC $_{\text{max}}$ = 33 g/100 g)
	Loamy sand (pH 5.8, C $_{\text{org}}$ 0.9%, clay 3%, K $_{\text{OC}}$ 2125, WHC $_{\text{max}}$ = 33 g/100 g)
	Loamy sand (pH 6.6, C $_{\text{org}}$ 0.9%, clay 3%, K $_{\text{OC}}$ 2125, WHC $_{\text{max}}$ = 33 g/100 g)

^a From Reference 7.

^b WHC $_{\text{max}}$ = maximum water-holding capacity.

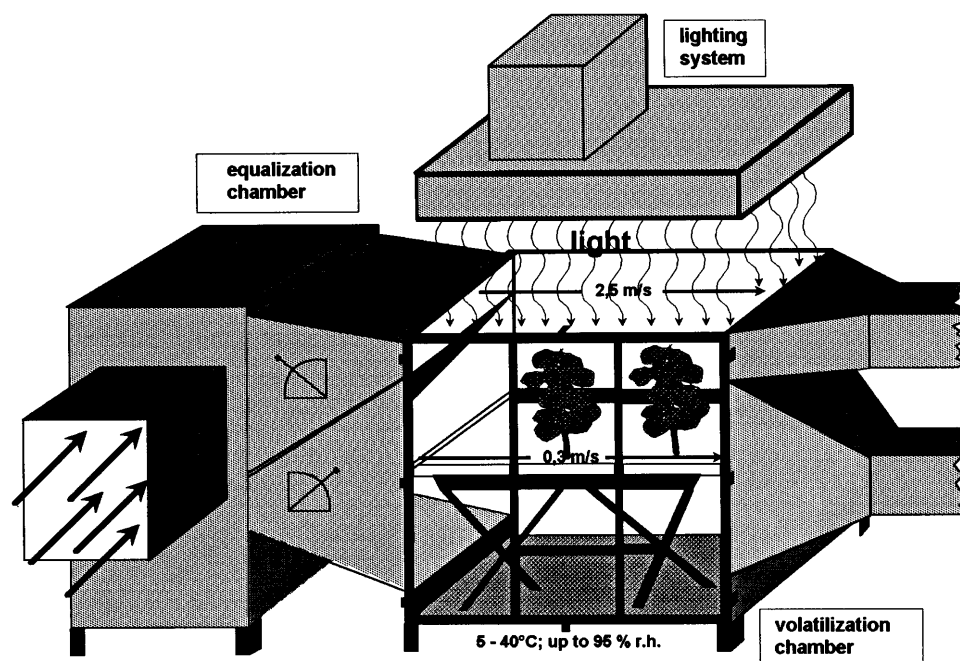


Fig. 1. Volatilization chamber (width: 1.0 m; depth: 0.8 m; height: 1.27 m).

metabolites collected in freezing traps and in $[^{14}\text{C}]$ carbon dioxide-traps (2-aminoethanol + phenylethylamine + diethylene glycol monobutyl ether + 1,2-dihydroxyethane, 1 + 1 + 1 + 1 by volume) for measuring mineralization. The PU-foams were changed 1, 3, 6, 24 hours (experiments with the same soil but different

pH) and 1, 3, 6, 24, 48, 72, 96 hours (experiments with different soils), after application of $[^{14}\text{C}]$ fenpropimorph and extracted with methanol (1 litre). With the analysis of the ^{14}C -residues in the soils at the end of each experiment, a total balance of the initial radioactivity applied was possible. To set up these mass balances,

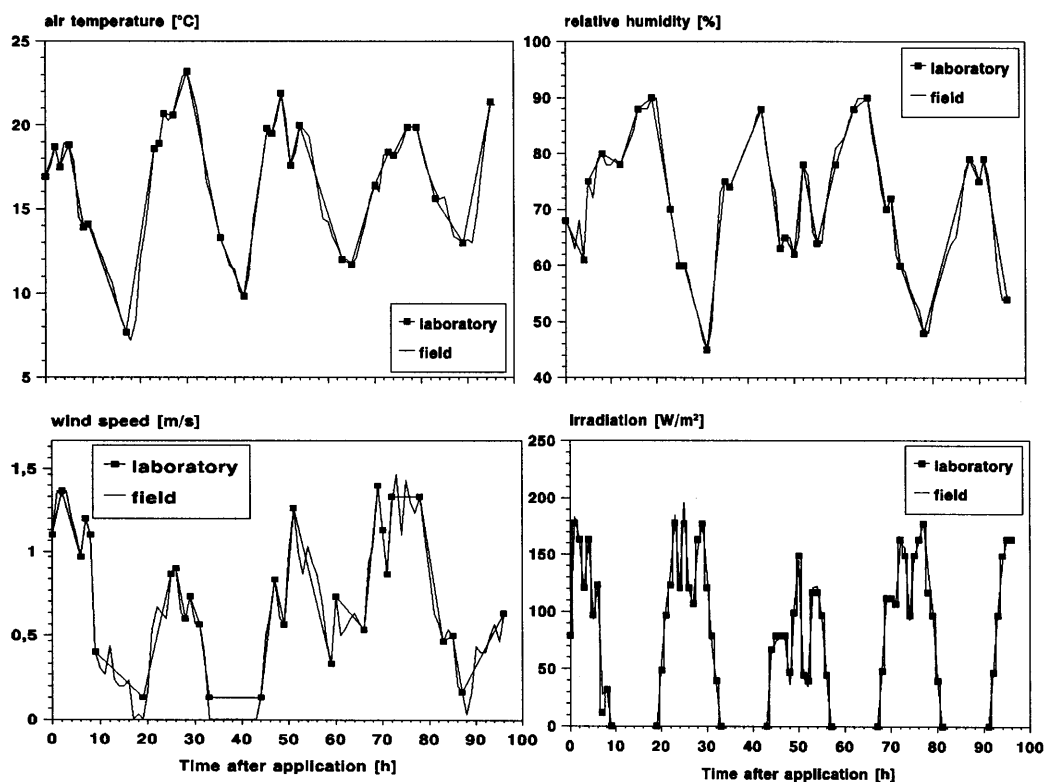


Fig. 2. Climatic conditions measured during outdoor studies with $[^{14}\text{C}]$ fenpropimorph, simulated and reproduced in the volatilization chamber during the experiments with three different soils.

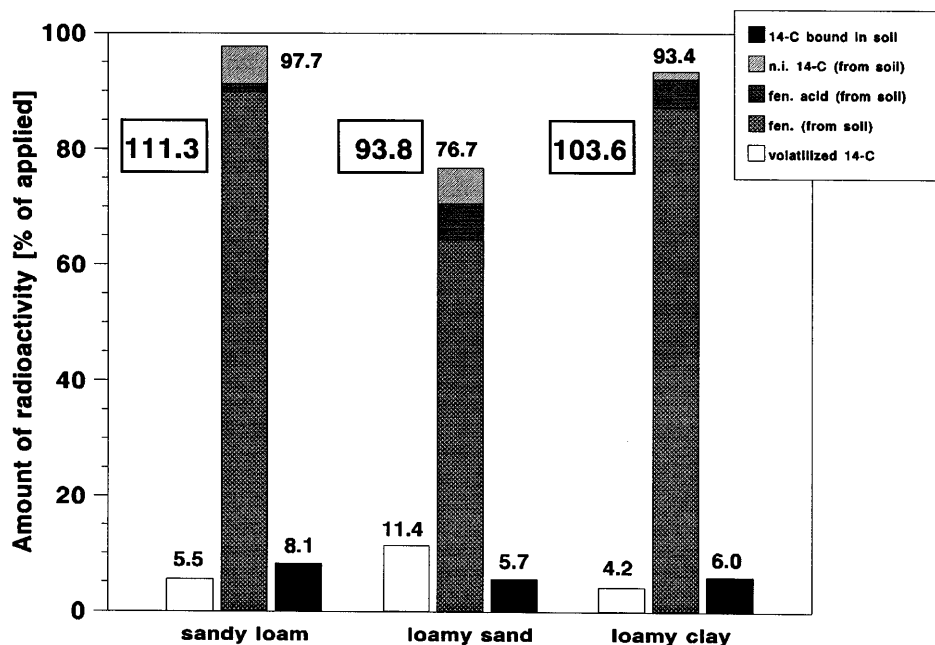


Fig. 3. Mass balances of volatilization experiments with [^{14}C]fenpropimorph 96 h after application to three different bare soils.

the soil was taken from the platforms at the end of experiments with different soils, homogenized and extracted for 3 h in duplicate with a Bleidner apparatus.¹ For the standard experiments with the same soil but different pH values, the soil samples were extracted for 2 h with methanol. Radioactivity remaining in the samples after exhaustive extraction was quantified after combustion using an oxidizer (Packard, 307). The ^{14}C -activity of all extracts was determined by an LSC 2550 TR/LL (Canberra Packard) and suitable scintillators. [^{14}C]Fenpropimorph (retention time: 15.2 min) and metabolites were identified by HPLC (Pharmacia, Sweden) using a Lichrospher column (100 RP-18, Merck) and aqueous ammonia 2.5 g litre⁻¹. A Flo-One/Beta Radio-HPLC Detector A-525 (Canberra Packard) was used for the detection of the ^{14}C -labelled analytes.

3 RESULTS

3.1 Volatilization under simulated outdoor conditions

Figure 3 shows the mass balances four days after application of the ^{14}C -labelled fenpropimorph formulation to three different soils. Most of the radioactivity applied still remained in the soils at the end of the experiments. Most of it was identified as [^{14}C]fenpropimorph by radio-HPLC. In addition to unchanged fenpropimorph, the main degradation product, [^{14}C]fenpropimorph acid, and other unidentified polar metabolites could be detected in all soils. Moreover, 3.3% and 1.1% of the

initial total radioactivity were mineralized to volatile [^{14}C]carbon dioxide in the experiments with sandy loam and loamy clay, respectively. In addition, bound residues (6.6% on average) were determined by combustion.

2.2% (experiment with sandy loam), 11.4% (experiment with loamy sand) and 3.1% (experiment with loamy clay) of the applied radioactivity could be extracted from the polyurethane foams of the air-sampling system and identified as [^{14}C]fenpropimorph. No metabolites were found in the PU foams or freezing traps.

In experiments with loamy clay and loamy sand, volatilization of the fungicide ceased 6 h after application (Fig. 4). However, the experiment with loamy sand indicates that, even four days after the treatment, the volatilization processes continued.

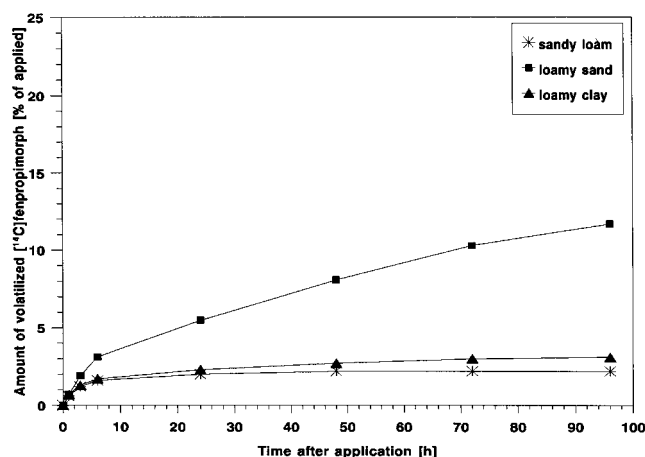


Fig. 4. Kinetics of volatilization experiments with [^{14}C]fenpropimorph applied to three different bare soils.

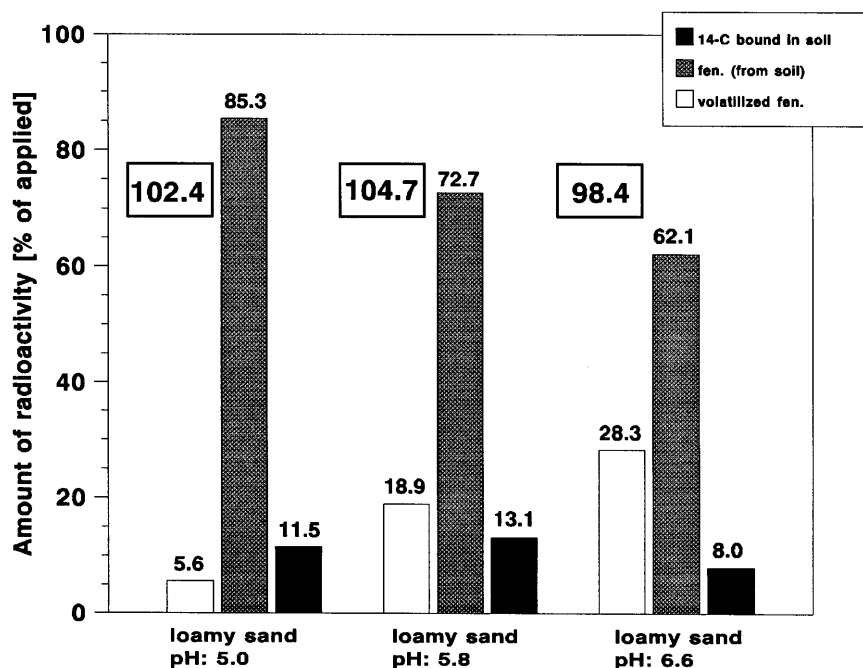


Fig. 5. Mass balances of volatilization experiments with $[^{14}\text{C}]$ fenpropimorph 24 h after application of three soils (loamy sand) with different pH values.

3.2 Volatilization under standard climatic conditions

Three experiments with the same soil but different pH (loamy sand pH 5.0; loamy sand pH 5.8; loamy sand pH 6.6) were carried out under standard climatic conditions without lighting after application of $[^{14}\text{C}]$ fenpropimorph to the soil surface. The experimental time was 24 h. The PU foams were changed 1, 3, 6 and 24 h after application. The results of the three experiments are given in Fig. 5. Twenty-four hours after application, the amounts of volatilization were 5.6% (loamy sand pH 5.0), 18.9% (loamy sand pH 5.8) and 28.3% (loamy sand pH 6.6). Extraction of the soil with methanol recovered 85.3%, 72.7% and 62.1% of the

applied radioactivity. Taking into account the combustion of the extracted soils (11.5%, 13.1% and 8.0%) the mass balances of the experiments were 102.4%, 104.7% and 98.4%.

The volatilization kinetics of formulated $[^{14}\text{C}]$ fenpropimorph from three loamy sands with different pH values are shown in Fig. 6. In all experiments the extracts were investigated by radio-HPLC. No metabolites were found in the PU foams or soil extracts from these experiments.

4 DISCUSSION

The volatilization of $[^{14}\text{C}]$ fenpropimorph was influenced by the soil properties. In the two series of experiments described above, two important processes became evident which limit the volatilization of $[^{14}\text{C}]$ fenpropimorph from soil surfaces:

The first competing process is the sorption of the fungicide to soil. Somasundaram *et al.*⁹ showed that the sorption of organic compounds is significantly correlated to soil properties such as pH value, clay content, organic matter or field moisture. In this connection the pK_a value (6.98) of fenpropimorph is important. As soil pH shifts to a value near or above the pK_a , increased sorption of basic pesticides to both soil organic matter and soil minerals is to be expected.^{10,11} Therefore an enhanced organic C and clay content led to very low volatilization rates of $[^{14}\text{C}]$ fenpropimorph from the

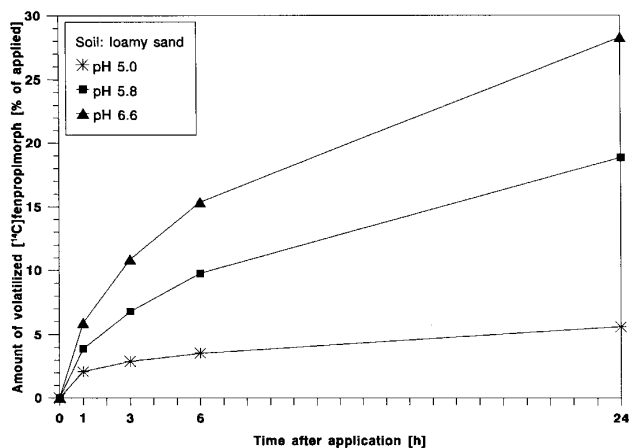


Fig. 6. Kinetics of three volatilization experiments with $[^{14}\text{C}]$ fenpropimorph applied to loamy sand with different pH values.

sandy loam and loamy clay adjusted to a constant soil humidity of 50% WHC_{max}. Thus, particularly the high K_{oc} values for fenpropimorph (Table 1) lowered the vapour pressure of the fungicide in soil. As a consequence, the comparatively higher volatilization of the fungicide from the loamy sand was due to the reduced amount of fenpropimorph-adsorbing organic C and clay components. The low volatilization rates of [¹⁴C]fenpropimorph from soils correspond with former studies which resulted in longer half-lives of pesticides on soil surfaces than on leaves.^{3,12,13}

The second competing process is the transformation of the organic compound to the essentially non-volatile salt with decreasing soil pH. Thus in standard experiments a loamy sand (50% WHC_{max}) was investigated which only differed in pH values. Lower pH values decreased the volatilization rate of [¹⁴C]fenpropimorph. The decreasing amounts of volatilization over 24 h ranging from 28.3% (pH 6.6) to 5.6% (pH 5.0) of the applied radioactivity, are based on a reduction of the volatile neutral form of [¹⁴C]fenpropimorph in the sandy soils. In this soil the organic carbon and the clay contents were too low to have a decisive effect on volatilization. When the pH values were almost identical, as in the experiments with loamy sand under simulated outdoor conditions (pH 6.1) and under standard climatic conditions (pH 5.8), the difference in clay content became more significant.

Furthermore, the competition of water molecules with fenpropimorph for sorption sites became more significant in the moist loamy sand (50% WHC_{max}), which is in accordance with various studies which postulate a much higher volatilization from moist soils than from dry soil surfaces.^{14,15}

By embedding the irrigation system in the soil, a continuous movement of water to the soil surfaces by evaporation during the experiments was induced. Thus, the upward capillary flow of water obviously led to increased volatilization of [¹⁴C]fenpropimorph in the case of the loamy sand by releasing the displaced pesticide molecules from the moist soil surface to the air.

Figures 3 and 5 characterize the volatilization kinetics of formulated [¹⁴C]fenpropimorph from different soils obtained by replacing and investigating the polyurethane foams 1, 3, 6, 24 (in the case of experiments under standard climatic conditions) and additionally 48, 72 and 96 h after spraying (in the case of experiments under simulated outdoor conditions). In the first hour after application the volatilization rates of all experiments were nearly the same. During this time the loss kinetics are primarily dictated by volatilization of the pesticide from the liquid phase of the spray solution.⁶ Therefore, the volatilization of fenpropimorph was then determined by Henry's Law constant (K_H) and the vapor pressure rose to values close to that of the pure compound. In the experiments with sandy loam and with loamy clay, the strongly adsorbing surface was

responsible for the stagnation of volatilization after six hours.

In the experiments with loamy sand, water evaporation from the soil significantly affected the volatilization behaviour of [¹⁴C]fenpropimorph, resulting in increased volatilization with time. This is in accordance with experimental data and model predictions assuming that accelerated volatilization of pesticides with K_H far below 2.65×10^{-5} ('Category III compounds') is controlled by the air-boundary layer thickness above the soil surface and the water evaporation rate.¹⁶ The measured curve of [¹⁴C]fenpropimorph volatilization from loamy sand in these experiment indicates that, at the end of the experiments, volatilization was still continuing. A prolongation of the experimental time would lead to an increasing amount of volatilized [¹⁴C]fenpropimorph. In this context it is interesting to note that the s-triazine prometon volatilized continuously from soil surfaces for a period of 14 days under conditions of evaporating.¹⁷ Similar results have been reported from studies investigating the volatilization behaviour of pesticides from soil surfaces.¹⁷ Hinderberger¹⁸ showed that rewetting processes increased volatilization of formulated [¹⁴C]diflufenican, [¹⁴C]isoproturon and [¹⁴C]vinclozolin after application on a loamy sand. In these experiments the volatilization of the investigated pesticides was not complete four days after application.

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